

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Process for the Catalytic Reformation of Petroleum Hydrocarbons

We, VEB LEUNA-WERKE "WALTER ULBRICHT", a nationalised Corporation organised and existing under the laws of Eastern Germany, of Leuna, near Merseburg, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The continuing development of petrol engines for the purpose of obtaining the optimum degree of economy in use has resulted in continually higher compression ratios in these engines. This is the reason for the ever

15 greater demands made on the fuels burned in them, where non-pinking properties are concerned. It is particularly within this last decade, for example, that numerous processes have been developed for the purpose

20 of converting (that is to say, reforming) the chemical contents of the petrols in such a way as to ensure that account can be taken of the need for the maximum possible resistance to knocking (maximum octane number). Unlike the first industrial reforming processes, which were carried out by purely thermal means without the use of catalysts, these methods are proving more and more

25 suited to the requirements of present day engines, an object which can only be attained with the use of highly active catalysts. From among the many catalytic substances or mixtures which guide the chemical conversion of the petroleum hydrocarbons in the desired direction and accelerate this process, such catalysts as  $\text{MoO}_3/\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ , Co-molybdate, and in recent times, particularly those catalysts which have a platinum content, have proved

30 especially suitable.

Metallic nickel cannot be used for such processes as it loosens both the C-C bond and the C-H bond, thus resulting in the formation of carbon, hydrogen and methane. Under the operating conditions re-

quired, the nickel is soon inactivated by products rich in olefins, even in the presence of hydrogen.

Ample tests have nevertheless been made to use nickel as well, this being a cheaper material. At quite an early stage, for example, the use of nickel in the form of a sulphide or oxide, alone or mixed with sulphides or oxides of the heavy metals of the first and/or eighth group of the 55 Periodic System, was proposed for the hydrogenation or dehydrogenation and also refining of industrial petroleum hydrocarbon mixtures. In certain cases catalysts of this kind, with a nickel content, were given additions of irreducible oxides, such as zirconium, thorium or cerium oxide.

All the aforementioned catalysts, when used for reforming petrols, require more or less high hydrogen pressures, usually far 65 above 10 atm. Furthermore, none of them operate in the desired direction except at temperatures from about 450 to over 500°C. Under these conditions it is inevitable that as a result of gasification some of the product to be reformed is simply lost, as far 70 as its actual purpose is concerned. Some of the catalysts with a nickel content which have been produced during the last few years, for example a catalyst with 98%  $\text{SiO}_2$ , 1%  $\text{Al}_2\text{O}_3$  and 1% nickel, operate 75 under similarly stringent conditions.

It has now been found, and it is the main characteristic of this invention, that petroleum hydrocarbons can be reformed with 80 catalysts containing metallic nickel without any appreciable gasification losses, if the catalysts employed are mixtures of metallic nickel and oxides of the elements of the second Group of the Periodic System. The 85 process is carried out at temperatures from 200° to 600°C., preferably 450° to 550°C., and at atmospheric pressure or increased pressures up to 75 atm., preferably up to 50 atm.

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It has also been found that the most suitable oxides of elements of the second Group of the Periodic System are zinc oxide and magnesium oxide. The most advantageous quantities for adding, range from 50 to 95 mol-%. It has been found that increased quantities of zinc oxide or magnesium oxide lead in particular, to the almost complete disappearance of the disintegrating tendency (leading to gasification-losses) of the metallic nickel and to a considerable intensification of the desired "reforming" effect of the catalyst.

It was surprising that the nickel-and-metallic-oxide catalysts found most suitable for the application on which the invention is based were those produced from the corresponding mixed oxalate- and/or formate-and/or carbonate-crystals. It was the use of just these catalysts produced from the mixed crystals that enabled undesirable subsidiary reactions, such as the formation of gas, to be largely reduced until they were overcome altogether.

The catalysts provided for in the invention can be given an addition of further carrier-substances, such as silicic acid, aluminium oxide, aluminium silicate, synthetic or natural earths, without rendering them any less effective, and these additives may if necessary have been treated with hydrohalic acid, particularly hydrofluoric acid.

#### EXAMPLE 1

A vertical pipe of 2 cm in diameter, with a perforated bottom, is given a filling of 25.5 cm<sup>3</sup> of a "pelleted" catalyst containing nickel and zinc oxide in a molecular proportion of 13:87. The catalyst was produced from the mixed carbonate powders, after "pelleting," by decomposition in the flow of hydrogen. 32 cm<sup>3</sup> of a benzene fraction with B.P. of 100°-130°C., together with 80 litres of hydrogen, is passed through this catalyst every hour at 350°C. The fraction was taken from a reaction-mixture resulting from the catalytic cracking of a petroleum product. This benzene contained 29.0% of olefins, 7.5% of aromatics, 33.0% of naphthenes, 30.5% of aliphatics, and had an Octane Number of 75.

After the catalytic thermal treatment, a benzene with practically unchanged boiling conditions is obtained, with a yield of 95.0% by weight. This benzene now only contains 4.0% of olefins; the content in aromatics has increased to 21.0%, while the naphthenes and aliphatics amount to 37.5% each. Despite the almost complete elimination of the olefins, the Octane Number has only decreased (by 3 units) to 72.

#### EXAMPLE 2

A nickel and zinc oxide catalyst, produced by the decomposition of the mixed oxalate crystals of both metals at 350°C. in the flow

of hydrogen, and having 90 mol-% of zinc oxide, is placed in the same apparatus as that used in Example 1. 15 cm<sup>3</sup> of the same benzene fraction, rich in olefins, together with 50 litres of hydrogen, is passed through 70 this catalyst every hour at 300°C.

98% by weight of the original product is recuperated. The reformed benzene contains 2.5% of olefins, 27.5% of aromatics, 38.0% of naphthenes and 32.0% of aliphatics. The Octane Number is 76.

#### EXAMPLE 3

The original product used in Examples 1 and 2 is freed of its olefinic hydrocarbon content by careful treatment with sulphuric acid. The resulting hydrocarbon mixture now contains 1.0% of olefins, 10.5% of aromatics, 46.0% of naphthene, 42.5% of aliphatics and has an Octane Number of 63. This benzene fraction, which is practically free of olefins, is treated in the same apparatus and under the same conditions and with the same catalyst as in Example 2. With just as high a yield as before, a benzene with the following composition is obtained: 2.0% olefins, 31.5% aromatics, 26.0% naphthenes, 40.5% aliphatics. The Octane Number was found to have increased (by 20 units) to 83.

A comparative test which was carried out under exactly the same conditions, but in which pure metallic oxide (produced from oxalate) was used instead of the aforementioned catalyst, resulted in the formation of hardly any liquid reaction product. Almost the whole of the original product used was decomposed into methane, this process being accompanied by the development of considerable heat.

Further comparative tests, with a nickel-alumina catalyst and a nickel-manganese-oxide catalyst, led to the same result: complete decomposition into gaseous hydrocarbons.

#### EXAMPLE 4

The operation was carried out under the same conditions and with the same product as in Example 3. The only point of difference is that the catalyst with a nickel content contains magnesium oxide in place of zinc oxide, in the same molecular ratio, the magnesium oxide in this case being produced from the corresponding mixed formate crystals. With only a very slightly lower yield, this results in the production of a benzene with practically the same composition as the hydrocarbons. The Octane Number is 80.

#### EXAMPLE 5

With the use of a catalyst which, in addition to 90 mol-% of zinc oxide (based on the quantity of nickel), also contains 16.4% by weight of SiO<sub>2</sub>, a benzene with an Octane Number of 81 is obtained, after the same treatment as in Examples 2-4, and about the same yield.

## WHAT WE CLAIM IS:—

1. In a process for the catalytic reformation of petroleum hydrocarbons, if necessary in the presence of hydrogen, at temperatures from 200° to 600°C., and at atmospheric or increased pressure, characterised by the use of catalysts consisting of mixtures of metallic nickel and oxides of the elements of the second Group of the Periodic System.
2. Process in accordance with Claim 1, characterised in that the catalysts contain the oxides of the elements of the second Group of the Periodic System in quantities of at least 20 mol-%, preferably 50 to 95 mol-%.
3. Process in accordance with Claim 1 or 2, characterised in that zinc oxide and/or magnesium oxide are used as the oxides of the elements of the second Group of the Periodic System.
4. Process for the catalytic reformation of petroleum hydrocarbons over a Nickel/Magnesium oxide or Nickel/zinc oxide catalyst at temperatures from 200°C. up to above 500°C. at atmospheric or increased pressures and if necessary in the presence of hydrogen.
5. Process in accordance with Claims 1 to 4, characterised in that the catalysts are produced from the corresponding mixed oxalate, and/or formate, and/or carbonate crystals.
6. Process in accordance with any of the Claims 1 to 5, characterised in that the catalysts are given an addition of further carrier-substances, such as silicic acid, aluminium oxide, aluminium silicate, synthetic or natural earths, which said carrier-substances may have been treated with hydrohalic acid.
7. Process as claimed in Claim 6, wherein hydrofluoric acid is used.
8. Process for the catalytic reformation of petroleum hydrocarbons, substantially as herein described.
9. Process for the catalytic reformation of petroleum hydrocarbons substantially as herein described in any one of the examples.
10. Petroleum products when produced in accordance with any one of the above claims.

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